

# A Comparison of Modifications Induced by Heat-Treatment and $\gamma$ -Irradiation in Spectroscopic Properties of Silica-Gel Thin Film Doped with Nd<sub>2</sub>O<sub>3</sub>

S. Bahammam, S. Abd El All, F. M. Ezz-Eldin

**Abstract**— Thin SiO<sub>2</sub> silica-gel film doped with 1mol.% Nd<sup>3+</sup> ions has been synthesized using tetraethyl-orthosilicate (TEOS) and neodymium nitrate as precursor sources of silica and neodymium oxides. The amorphous nature of gel glasses has been confirmed by XRD spectra. XRD investigation shows that both low (500oC) and high (1150oC) heat-treated samples to be amorphous indicating that the Nd ions are incorporated in the SiO<sub>2</sub> network. Both temperature and  $\gamma$ -radiation-dependent spectroscopic properties of Nd<sup>3+</sup> ions in silicate glass were studied. As the temperature increases, the optical absorption (O.A.) intensity of Nd<sup>2+</sup> increases sharply. However transmission% (T%) decreases sharply except at maximal temperature (1150oC) where it is completely increased. Optical absorption spectra (UV-vis) of the samples before and after  $\gamma$ -irradiation show generation of new broad band below 500 nm (390–458nm) along with dips in the spectrum at the location of main Nd<sup>3+</sup> absorption lines at maximal heat-treatment temperature (1150oC). This is attributed to the generation of different types of defects in the glass matrix along with possibility of change in the valence state of Nd<sup>3+</sup> to Nd<sup>2+</sup>. The behavior of both O.A. and T% spectra of the irradiated samples designates a strong dependence with gamma radiation doses, where the magnetic dipole transition 5D<sub>0</sub>→7F<sub>1</sub> of the Nd<sup>3+</sup> ions presents huge defects for irradiation doses up to 18 kGy. FTIR absorption spectra of these glasses are found to be dominated mainly by the characteristics silicate groups and water (OH) present in the glass network. The effects of temperature on IR absorption are observed in the form of bond breaking and possible re-arrangement of bonding. However,  $\gamma$ -irradiation produces minor effect on the IR spectra which can be related to the shielding behavior of the glass. The generation and bleaching of irradiated sol gel glass were found to permit the creation and reduction of the larger part of Nd<sup>3+</sup> or Nd<sup>2+</sup> ions respectively in the glass. This study also shows the usefulness of this sol-gel glass as yes or no dischargeable irradiation detector, due to the remarkable color change after irradiation, which persists for a long time (up to 20 days).

**Index Terms**— Silica-Gel; Nd<sub>2</sub>O<sub>3</sub>; XRD; UV-Vis; T%; FT-IR; heat-treatment;  $\gamma$ -rays

## I. INTRODUCTION

The sol-gel chemistry permits glasses to be prepared at a much lower temperature than the conventional melt glass

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techniques. Besides, it allocates higher doping concentrations and an extra homogeneous distribution of neodymium in the glass host matrix to be attained. The utilization of sol-gel derived silica as a glass host for laser applications necessitates the fulfillment of some decisive factors comprising high density, high mechanical and thermal shock resistance, compositional purity and optical grade superiority. Study of glasses doped with lanthanide and transition metal ions have been found to attract much interest owing to its significant optical properties, higher thermal expansion coefficients and minor transition temperature [1–5]. Along with the promising hosts for Nd<sup>3+</sup> ions, glass matrices exhibit several advantageous properties to recognize them as more valuable and controllable host materials. This may be due to their distinctive properties such as preparation, fabrication, good mechanical and thermal stability, low price and companionable thermal conductivity [6-9]. Thermal heat-treatment of the doped gels modifies the local environment of the metal ions due to diverse reasons resulting in fluorescence spectra. Although this behavior is general for most of the modifier ions doped gels studied, a detailed study of the integration of Nd<sup>3+</sup> ions in sol-gel silica host is yet to be well launched. As the optical properties of the doped silica systems depend on the neighboring arrangement and bonding of the dopant cations [10], a detailed understanding of the structural development during the gel to glass conversion of Nd<sup>3+</sup>-doped silica gels is very significant to fabricate the material for optical applications. The densification of the gel is evidently caused by breaking and reforming bonds in the silicate networks and the properties of the gel become similar to those of conventionally prepared glass. On heating, the gel loses trapped volatiles below 200oC and a subsequent monotonic loss with heat treatment temperature due to the removal of hydrogen bonded molecular water and dehydration via condensation of silanol groups [11]. It has been founded that the majority of the glasses produce various interesting revolutionizes in their properties, when irradiated by high energy particles or radiation such as neutrons, UV, and gamma-rays[12]. The irradiation effect generates changes in the optical properties of glasses in the form of creation of some new induced absorption bands. In recent times a chain of studies have been accounted on  $\gamma$ -irradiation effect on diverse types of glasses such as soda lime phosphate, cabal, bioglass, borosilicate, lithium borate and phosphate glasses [13-15], where intrinsic defects are found due to occurrence of dopants or impurity in the glass. The

results of radiation damage in glass are classified into three classes: atomic displacement by momentum and energy transfer; ionization and charge trapping; radiolytic or photochemical effects. These special effects are associated with the energy of radiation, as well as the entirety dose [16]. Trapping of an electron avoids staining of optical glasses that have transition elements. These electrons produce new induced colors with irradiation. The ionizing radiation generates bound electron-hole pairs (excitons). Exposure to gamma irradiation results in atomic displacements or broken bonds by radiolytic or knock-on displacements. Color centers are produced from trappings of the electrons and holes at the damaged sites [17-19]. The study of structural environments around the rare-earth ion is necessary to be aware of the optical absorption and luminescent properties of rare-earth ion-doped glasses [20]. A number of the dopants such as transition metal ions or lanthanide ions dopants confines negatively charged electrons or positively charged holes generating a modification in their valence state through photochemical reaction through the exposure to successive  $\gamma$ -irradiation.

Absorption spectroscopy is an important tool in the inspection of materials. Just a superficial view of the absorption vs. the wavelength and the absorption edge is sufficient to tell whether the material under investigation is crystalline or amorphous in nature. The absorption edge is extremely sharp in crystalline substances whereas it has a limited slope in amorphous substances. This method can also offer information about the optically induced transitions, the band structure, and the band gap of materials [21]. Discrepancy in the optical band gap of silicate glasses has formerly been studied as a function of radiation composition [22].

Heat treatment and irradiation at different temperatures and  $\gamma$ -doses respectively were applied. The SiO<sub>2</sub>-Nd<sub>2</sub>O<sub>3</sub> thin film obtained was analyzed by X-ray diffraction (XRD), Optical (UV-Visible) absorption, transmission% and FTIR spectroscopy in order to determine their global, local and electronic structures. Preliminary results of gamma-radiation detection using the optical absorption enhancements of the neodymium excited states were present. The resistance of bands intensity during moderate environmental conditions was also studied.

## II. EXPERIMENTAL

### A. Preparation of Silica Gel Thin Film

Neodymium oxide films were deposited by a spin-coating process. The Nd<sub>2</sub>O<sub>3</sub> films were prepared on ITO conductive transparent glass and Corning glass (2947) substrates. The substrates were cleaned with detergent and flushed with copious amounts of de-ionized water. The substrates were consecutively rinsed with acetone, methanol and isopropyl alcohol and dried in air.

For the preparation of silica gel thin film, tetraethylorthosilicate (TEOS) (Fluka purum grade), was diluted with ethanol (CH<sub>2</sub>CH<sub>3</sub>OH), then hydrolyzed with water using HCl catalyst, with molar ratios

0.028:0.1305:0.187:0.0823. 1Mol.% Nd<sub>2</sub>O<sub>3</sub>. Neodymium oxide was introduced by adding a mixture of neodymium nitrate initially dissolved in distilled water to the solution. Then the final solution was filtered, followed by steering for one hour at room temperature. The resultant homogeneous solutions were spun on silica glass substrate at around 3500 RPM for 30 second. After deposition the films were aged for 72 hours at about 60°C in the drying oven. The densification of the prepared gel samples were obtained by heating in air for two hours at different temperatures ranging from 500 to 1150°C in a programmable furnace with the rate of 3°C/h.

### B. X-ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns of the prepared samples were recorded with Philips X-ray diffractometer PW/1710; with Ni filter, with monochromatised CuK $\alpha$  radiation of wavelength 1.5418Å at 40 KV and 30 mA. The peak profile recorded with good resolution, 1/8 deg/min., was performed and the approximate crystallite sizes at FWHM were determined from the X-ray diffraction data using the Scherrer formula ; ( $G = \lambda / D \cos \theta$ ) where G is the grain size,  $\lambda$  is the wavelength of the X-rays (1.5418), D is the width of the peak at half maximum and  $\theta$  is the angle of incidence of X-ray beam.

### C. Optical Absorption Measurements

The absorption and transmission spectra of the fresh and irradiated samples were recorded on a Perkin-Elmer Lambda 6 UV/VIS spectrometer, 101C/min. covering the wavelength range 190 to 900 nm. The glass specimens were measured before and immediately after been irradiated for successive irradiation doses (3, 8 and 18 kGy) at room temperature. Fading measurements were carried out for irradiated glass (18kGy) at room temperature (~25oC) after different intervals of time up to 7 days.

### D. Infrared Absorption Measurements

FTIR measurements were carried out through the KBr disc technique in the wave number range 4000 – 400 cm<sup>-1</sup> using a Fourier transform infrared spectrometer (type :Jasco FT/IR – 430, Japan). 2 mg of finely pulverized samples with 200 mg of KBr and subjected them to a load of 5 tons/cm<sup>2</sup> for 2 minutes to produce clear homogeneous discs. The IR measurements were immediately carried out for the discs before and after irradiation.

### E. Irradiation Procedures

All the glass samples were then finely powdered using a clean agate mortar pestle. The prepared samples were subjected to a series of three radiation doses of 3, 8 and 18 kGy using <sup>60</sup>Co source of gamma radiation at NCRRT, Egypt. The glass samples were irradiated for required time interval to achieve the desired overall dose. The dose rate was 2.08 kGy h<sup>-1</sup>. All the powdered glass samples were wrapped in butter paper and then packed in polythene sachets before irradiation.

### III. RESULTS AND DISCUSSION

#### A. XRD Measurements

The alkoxide sol-gel process is an efficient method to prepare silicate matrix by the hydrolysis of alkoxide precursors followed by condensation, to yield a polymeric oxo bridged SiO<sub>2</sub> network. The advantages of this technique are the homogeneity and the purity of the gels associated to a relatively low sintering temperature. XRD- The shift in the diffraction lines might be attributed to the larger radius of the dopant ion, compared to the ionic radius of the Si ion, which may cause an expansion of the lattice parameters in the Nd<sup>3+</sup> doped silicate nanomaterials.

The starting solutions, from which these samples are produced, have a high H<sub>2</sub>O/TEOS ratio and produce an amorphous SiO<sub>2</sub> structure with some structural similarities to the cristobalite. Addition of Nd<sub>2</sub>O<sub>3</sub> form metal oxide aggregates, but the amorphous SiO<sub>2</sub> structure does not crystallize after thermal treatments at temperature up to 1150oC.

The effect of different sintered temperature on the structure of the prepared silica gel doped with Nd<sup>3+</sup> (G500 & G1150) is shown in Fig. 1. This figure shows XRD patterns of G500 and G1150 samples sintered at 500 and 1150oC for 2 hours. No peaks are observed in samples heated at 500oC except the hump at 2θ between 12 and 24oC attributed to amorphous silica gel. However, small and broad peaks at 2θ equal about 24o were superimposed on the mentioned hump appeared by heated the sample at 1150oC for 2 h, which may be ascribed to preliminary crystallization of samples and can be indexed as (110) diffraction principal line of tetragonal α-cristobalite. Other peaks superimposed on the amorphous hump were detected at 2θ equal to 23.62, 26.4, 28 and 29.9 indexed as (111), (102) (112) and (112) diffraction line of tetragonal α-cristobalite, respectively. These results are an indication of the beginning of crystallization at 1150oC. This is in agreement with Bouajaj and Ferrari [23] who suggested that at 1050oC is the beginning of crystallization, where at 1150oC the crystallization occurs [24,25].

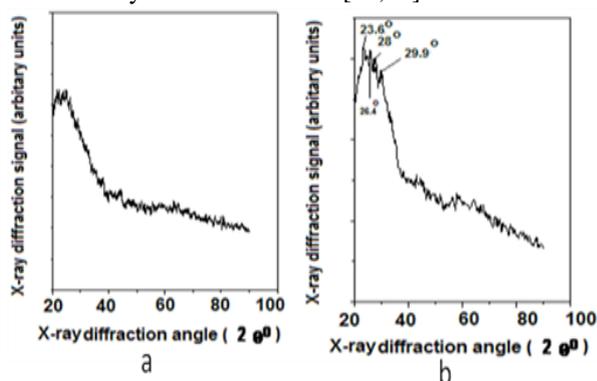


Fig. 1 XRD patterns of silica gel doped with 1 % Nd<sup>3+</sup> ions; 1a- sintered at 500oC (G500) and 1b-1150oC (G1150) samples

#### B. OPTICAL MEASUREMENTS

##### 1) Effect of Different Heat-Treatments

Effect of Different Heat-Treatments on Optical Absorption It is well known that, thermal treatment concurrently leads to the densification of the gels. At intermediary temperatures,

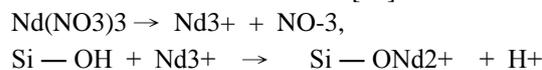
the host structure exhibits inhomogeneity due to inadequate formation of siloxane bonds. Further formation of Si-O-Si network at higher temperature (1150oC) causes destruction of water sites which causes advancement towards a glassy structure[11]. Recently, Langlet et al.[10] have reported that, DTA/TGA and FTIR studies indicated that, for the silica-xerogel doped Nd<sub>2</sub>O<sub>3</sub>, the oxide network formation was almost entire at about 500oC. Surpassing this temperature, the sample underwent a slow corresponding elimination of OH groups. One can see from Fig. 2a that, although the basic nature of the absorption spectra did not change after different heat-treatments (up to 1150oC). It can be noticed two regions of the spectra which are particularly modified by heat-treatment: 190– 320 nm first range (Fig. 2b) and 390–600 nm second range (Fig. 2c). Extinctions in the entire broad absorption band (~400-585) from the VIS to near-IR increase; the same be appropriates for the bands located in the UV region; two small peaks at ~208, 220 nm, broad band at ~230-240 nm and distinct peak at ~248 nm, all these bands overlap and forming two distinct broad band at ~225-230 and 243-248 nm accompanied with slight shift to longer wavenumber and decrease in their intensities when the sample was heat-treated at 850oC (G850). However, when the glass gel was heated up to 1000oC (G1000) the bands located in the first region were resumed to small peak at ~230 nm and two highly intense peaks at ~244 and 263 nm which are nearly equal and extremely shifted to longer wavenumbers accompanied with broadening in the band width (Fig.2b). The same trend was observed in the second region (390–600 nm) (Fig.2c). This results evidently points out that certain structural rearrangements have took place inside the glass matrix perform as a result of diverse thermal treatment, also this signifies that with the increasing temperature, the number of SiO<sub>4</sub> tetrahedra is increasing, leading to a stable glass. The extremely shift to longer wavenumber can be assumed to be related that, Nd<sup>3+</sup> ions are not incorporated into the skeleton consisting of SiO<sub>4</sub> tetrahedra in the gel but are present as [Nd(H<sub>2</sub>O)<sub>y</sub>(NO<sub>3</sub>)<sub>6-y</sub>](y-3)+ complex. As the densification of the gel proceeds, a condensation reaction between the silica gel particles takes place. This reaction shrinks the bulk gel and is assumed to yield some compressive stress at the [Nd(H<sub>2</sub>O)<sub>y</sub>(NO<sub>3</sub>)<sub>6-y</sub>](y-3)+ complex. Subsequently the Nd-O bond is forced to be shortened compared to the [Nd(H<sub>2</sub>O)<sub>y</sub>(NO<sub>3</sub>)<sub>6-y</sub>](y-3)+complex. As a result the interaction between the orbitals of the Nd<sup>3+</sup> ion and the orbitals of the ligand becomes large leading to the increase in the UV absorption with a shift of the absorption edge towards longer wavelengths. As the heat treatment temperature is increased the [Nd(H<sub>2</sub>O)<sub>y</sub>(NO<sub>3</sub>)<sub>6-y</sub>](y-3)+ complex reacts with the silica gel to release H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> ions, and Nd<sup>3+</sup> ions are then incorporated into the silica network[26].

It is accepted that, thermal treatment concurrently leads to the densification of the gels. At intermediary temperatures, the host structure exhibits inhomogeneity due to inadequate formation of siloxane bonds. Further formation of Si-O-Si network at higher temperature (1150oC) causes destruction of water sites which causes advancement towards a glassy structure[11]. The xerogel sample which was heat-treated at

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1150oC (G1150) shows a kink band with a peak at ~192nm and at the same time, a narrow obvious band at~ 200 nm which is shifted to extremely short wavenumber. For our case, increasing in the temperature two factors could be identified in general (i) A decrease in UV absorption with a shift of the absorption edge towards the shorter wavelengths (the higher temperature, the greater the shift) ; (ii) a progressive disappearance of the band located in the first region and a consequent decrease in the wavenumber. These two features are explicated in the following. In the gel, siloxane network or SiO<sub>2</sub> colloidal particles connected with each other which cannot co-ordinate Nd<sup>3+</sup> any longer due to their too large size, leaving Nd<sup>3+</sup> ions, H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> ions in the pores. Moreover, the drastic drop of absorption in the UV-region for the glass G1150 is assumed to have no serious conversions among Nd<sup>2+</sup>, Nd<sup>3+</sup> and Nd<sup>4+</sup> ions occurred, but rather a kind of the inter-diffusion process [27,28] of the dopants (incorporating Nd ions) and Si (from the neighboring cladding region of the perform) took place at maxima thermal heat-treatment at the complete stage, with the result being generally drop of intensity in all absorption spectrum. Adding together, this may be due to the totally hydrolyzed and no reesterification of the methoxy groups which occurs during drying. The shifting to shorter wavenumber can be assumed to be correlated with silanol groups in siloxane oligomers created in the sol which can co-ordinate with Nd<sup>3+</sup> ions all along with H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup>. Though, the size of the oligomers is too large that they cannot approach the Nd<sup>3+</sup> ion very closely causing less overlap between the orbitals of the Nd<sup>3+</sup> ion and the 2p orbitals of the oxygen atoms in the silanol, signifying a reduction in the ligand field strength.

maximal decrease up to 1000oC and then increases at higher temperature (1150oC). At such high temperature, the silica glass shows generally un-ruptured and optically transparent. When the glass transmission% is initiated to decrease with temperature (850 and 1000oC), the G500 glass sample is observed to drop partially its transparency. Such a behavior already cited by several authors [29-31] and is communicated to the little amount of hydroxyl groups remaining in the sample pores after heating at high temperature. During heating, hydroxyl groups are freed in the network pores in the form of water vapors (pyrolysis of SiOH groups and following water evaporation). Since the sample densifies, the collapse of pores avoids the complete elimination of remaining water vapors. Furthermore, at such elevated temperature(1000oC), the entrapped water vapors expand, resulting in pores bloating and/or sample fragmentation causing to form micropores within a dense glassy matrix, which influences dramatically the glass density and transparency. Conversely, at their maximal temperature (1150oC), the silica glass appeared generally unruptured and optically transparent, and the broad band at~ 325-394nm was reduced to a kink band with a peak at ~400nm. This irregular trend can be explained in terms of pH disparities during gelation. As gelation progresses, Si–O–Si bonds develop through hydrolysis/polycondensation and Nd nitrate molecules react with the developing network. Nd<sup>3+</sup> cations at high temperature are incorporated to the Si–O–Si network and occupy the proton site of a silanol species. The overall reaction can be written as follows [32]:



Thus, as protons (H<sup>+</sup>) are released in the solution while the reaction continues, the solution pH must be decreasing. According to Ref. [33], a lowering of the basic pH favors the formation of fewer branched oligomeric species and explains a better gel densification during the drying treatment. However, as the Nd assimilation in the silica matrix is probably to take place not only during solution preparation but also during the gelation, drying and heating stages, it is hard to suppose on the actual pH decrease of the solution. So, as shown in Fig. 3, the transmission% of gel at maximal temperature (1150oC) sintering treatment is more than the value measured at 850 and 1000oC, but remains considerably inferior to that of the G500 xerogel sample. From the previous results, it is evident that a high temperature sintering treatment would be necessary to reduce efficiently the hydroxyl content.

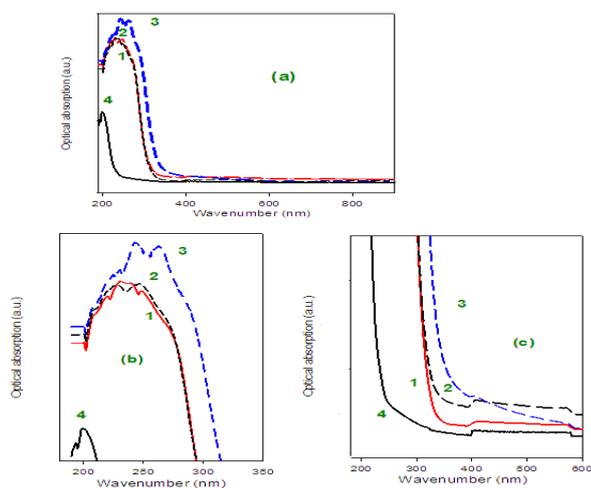


Fig. 2 Optical absorption of silica gel doped with 1 % Nd<sup>3+</sup> ions sintered at different sintering temperatures, 1- G500, 2- G850, 3- G1000 and 4- G1150 samples

### Effect of Different Heat-Treatments on Optical Transmission%

Fig. 3 shows the effect of different heat-treatment temperature (500, 850, 1000 and 1150oC) on the transmission% for the investigated glass. All the curves reveal similar transmission% performances. The transmission% decreases with temperature and attains a

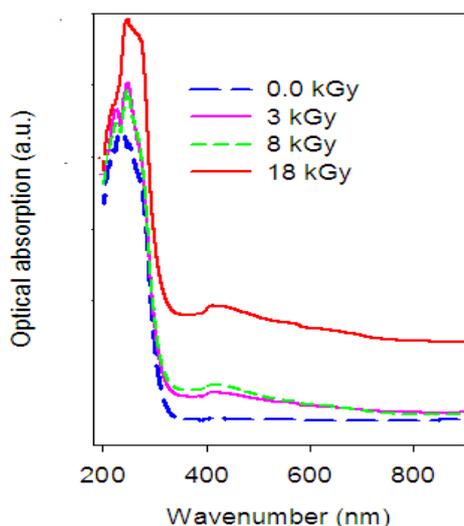


Fig. 3 Transmission % of silica gel doped with 1 % Nd<sup>3+</sup> ions sintered at different sintering temperatures

## 2) Effect of $\gamma$ -irradiation

The difference in the annealing behavior of the G500 and G1150 samples is also manifest if we study the effect of  $\gamma$ -irradiation on the absorbance and transmittance of the films following the anneal progression. At the same time as irradiation of the G500 films still generates at  $\sim 242$  nm and corresponding growth at 200 nm,  $\gamma$ -exposure of the G1150 films now no longer results in an overall increase or decrease of the UV absorbance as seen in the G500 case.

Radiation induced generation of point defects in silica is a timely research issue strongly motivated by the detrimental impact of defects in the optical transparency of silica in the (UV) range, widely exploited in applications, as well as by reasons of fundamental physical interest[34,35]. One of the most common defects induced in silica by irradiation is the paramagnetic E' center. The structural model of this defect consists in an unpaired sp<sup>3</sup> electron on a threefold coordinated Si atom (=Si●), and it can be detected either by observing its absorption band peaked at 5.8 eV (212-215nm) or its characteristic EPR signal[36]. Recently[37], experimental evidence has provided that the generation of E' center does not occur by direct interaction of radiation with precursors. In contrast, it takes by interaction of precursors with elementary excitations (excitons or free charges) initially produced by a two step process occurring on Nd impurity sites.

When the absorbed dose of the samples increased, the structures of the coatings changed from dense to porous, while the refractive-index of the irradiated samples decreased. It was thought that the porous structure could be produced by a variety of absorbed doses and different irradiation processes. It can be assumed that the higher absorbed dose greatly affected the optical and electrochromic properties of the coated Nd<sub>2</sub>O<sub>3</sub> films on ITO substrates than on the glass ones. Gamma irradiation generates three main optical density bands at  $\sim 230$ , 270 and 390–450 nm for the studied glass. These changes are related to the defect centers. The number of ion-trapping sites may increase due to the defect centers. Therefore, more protons accumulate in irradiated Nd<sub>2</sub>O<sub>3</sub> thin films. Figs. (4&5) and (6&7) show the

absorption and transmission spectra of the studied samples before and after different doses of gamma irradiation (3, 8 and 18 kGy). In comparison with unirradiated samples, the irradiated sol-gel glass sample G500 (Fig. 4), shows intense absorption of both at 250 and 400 nm peaks, in contrast there are remarkable decreases in optical transmission bands (370, 580 and 800nm) (Fig.6). The same trend appeared for G1150 prepared sample, (Fig. 5 & 7). This observation indicates that part of the Nd<sup>3+</sup> ions in the materials were converted to the (Nd<sup>3+</sup>)<sup>+</sup> during the gamma irradiation, i.e. the Nd<sup>3+</sup> acts as holes trap in this matrix. The intense absorption of Nd<sup>3+</sup> in the gamma-irradiated samples agrees with the assumption that the majority of the neodymium ions in the materials are in trivalent state [38]. Furthermore, the shift of the charge transfer band implies that the Nd<sup>3+</sup> ions are transformed to the higher valence states (Nd<sup>3+</sup>)<sup>+</sup>.

The observed decrease and increase in the absorption broad band intensities at  $\sim 460$  nm for sample G1150 shown in (Fig. 5), lead to the postulation that the Nd<sup>3+</sup> ions are responsible for the suppression of the absorption band induced in the visible at  $\sim 200$  nm. If this band is attributed to positive hole centers formed by loss of electrons from oxygen during the process of irradiation, then the electrons resulting from the reaction:  $\text{Nd}^{3+} + h\nu \rightarrow (\text{Nd}^{3+})^+ + e^-$  could annihilate the positive hole centers. Similar discussion resulted in the postulation that the 200 and 290 nm bands are also attributed to hole centers which may have different properties from those associated with 460 nm band [39]. The center associated with this band is tentatively designated as (Nd<sup>3+</sup>)<sup>+</sup> + e<sup>-</sup> in which the number of Nd<sup>3+</sup> ions and the number of electrons involved in the formation of the center are unknown. Moreover, irradiation for the glasses prepared by sol-gel technique causes dissociation of water leading to an increase in [OH], and causes a transient change in the anharmonicity of the well [12]. Besides that, irradiation causes removal of a proton (protonation) from alkyl radicals (GH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>••••) dissolved in the glass. In conclusion, the enhancement presented by the ions can be explained as a decrease of non-radiative pathway, where these pathways, mainly water molecule or O-H chemical bonds, are nearly eliminated by the irradiation [40].

The obvious decrease in intensity of absorption at intermediate dose (8 kGy) as showed in Fig. 5 may be due to severe disruption of bonds in the glass matrix that could result in defects rebonding in "normal" configurations. Because of the lack of spectral data, it is impossible to determine if this effect is due to one type of defect center or the interference of the tails of several absorption bands [12]. Another postulation can be introduced, that the observed decrease in intensity of the absorption spectra for some bands at low irradiation doses can be discussed as follows: the origin of this negative induced absorption may be attributed to the destruction of NBO's by irradiation, which would cause the absorption edge to shift to shorter wavelength [41]. These postulations are in good agreement with previous works [42,43]. Another suggestion may be advanced and is simply based on assumption that there are several color centers with different rates contributing to the absorption at a given wavelength. Another postulate may recognize that there are several

rate-determining processes operating concurrently during irradiation. Several authors had advanced similar conclusions [12,44].

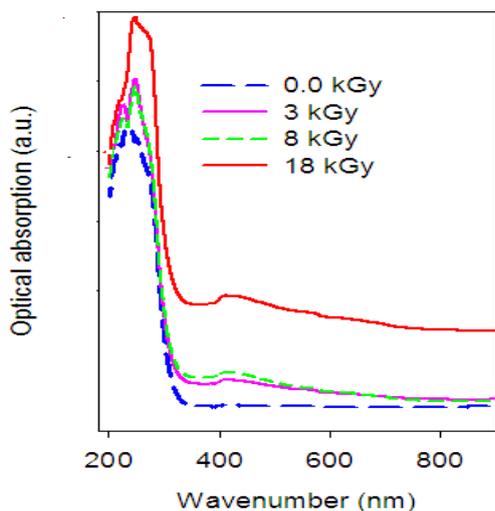


Fig. 4 Effect of different  $\gamma$  irradiation doses (3, 8 and 18 kGy) on the optical absorption of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 500oC (G500) sample compared to the unirradiated (0.0 kGy).

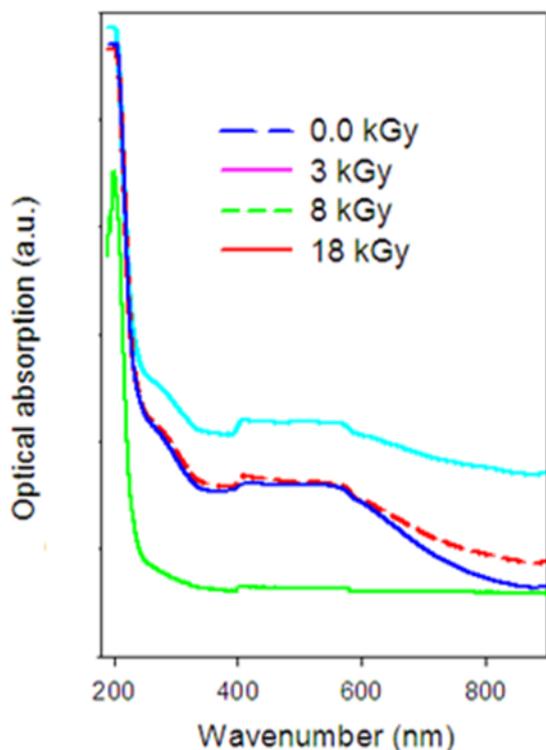


Fig. 5 Effect of different  $\gamma$  irradiation doses (3, 8 and 18 kGy) on the optical absorption of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 1150oC (G1150) sample compared to the unirradiated (0.0 kGy).

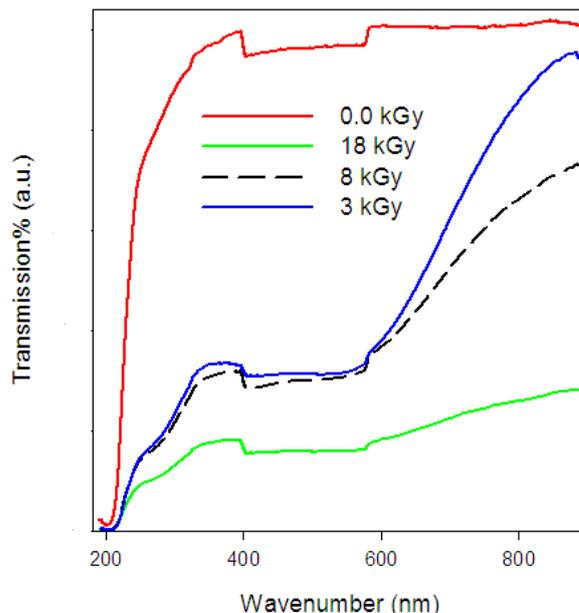


Fig. 6 Effect of different  $\gamma$  irradiation doses (3, 8 and 18 kGy) on the transmission% of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 500oC (G500) sample compared to the unirradiated (0.0 kGy).

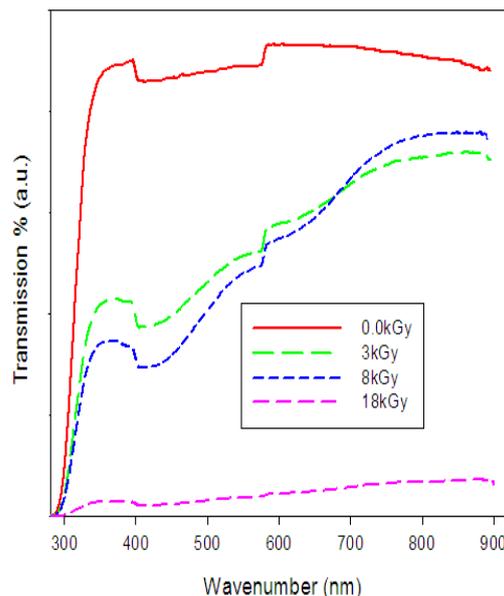


Fig. 7 Effect of different  $\gamma$  irradiation doses (3, 8 and 18 kGy) on the transmission% of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 1150oC (G1150) sample compared to the unirradiated (0.0 kGy).

### 3) Response Curves

We measured the optical absorption (O.A.) at ~240 and 420 nm were measured. Fig. 8 is a plot of O.A. as a function of the gamma irradiation doses. As seen in Fig. 8, the studied sol-gel indicates an initial fast growth of the absorption bands at ~240 and 420 nm then followed by a slight growth, and then increases as the dose is increased up to 18 kGy, and the magnitude of the absorption band at 240nm is higher, however it is more slowly at 420nm. These results can be recognized when it is supposed that the optical absorption in glasses of different chemical compositions is the result of

equilibrium between the creation and passivation of defect centers. This equilibrium is controlled by the polarizing power of the cations, the concentration of modifying ions, and the abundance of non-bridging oxygens [45].

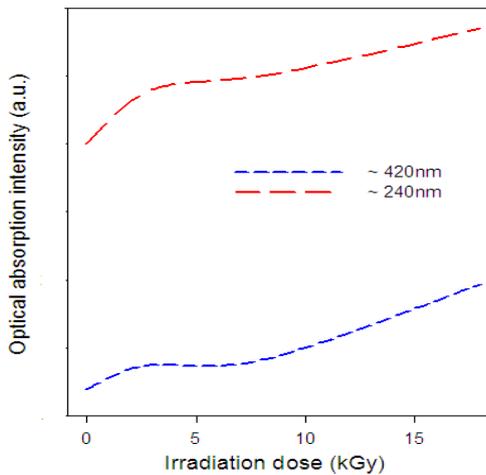


Fig. 8 Growth curves of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 500oC (G500) at wavenumber ~ 240 and 420 nm

#### 4) Post-Irradiation Stability

Figs. 9 and 10 show the passivation process during 20 days for the G500 and G1150 samples after been exposed to 18 kGy. In sequence to explicate the passivation process, it can be supposed that the damage process in sol-gel glass consists of principal generation of highly mobile electrons and holes originated by irradiation. These mobile electrons then either generate an electron scavenger or become localized over various groups. These localized or solvated electrons are dependable for the observed early decay after irradiation, which is practically well correlated with holes trapped on non bridging oxygen (NBO) atoms. Trapping of holes signifies that the neodymium ions are no longer bound by Columbic forces to oxygen atoms and are diffused away and entrap electrons. In addition, radiation annealing effect, which has been showed, consists of an actual annealing and annihilation of defect flaws rather than just a bleaching and depopulation of the trapped charge. The bleaching of the irradiated sol-gel glass causes slight fading at the beginning, but occasionally a limited increase in glass absorbance is noticed with further increase in the fading time. This may be due to the photo-oxidized (Nd<sup>3+</sup>)<sup>+</sup> defects in the sol-gel glass investigated, which can also be formed with the irradiation of sol-gel glasses and no recovery being detected, in contrast to the photo reduced (Nd<sup>3+</sup>)<sup>+</sup> defects, which are annealed to Nd<sup>4+</sup> by thermal treatment below the T<sub>g</sub> temperature. Another postulation of these bleaching experiments assumes that the 460 nm band is an electron trap since it bleaches out whenever one of the hole traps is bleached [46].

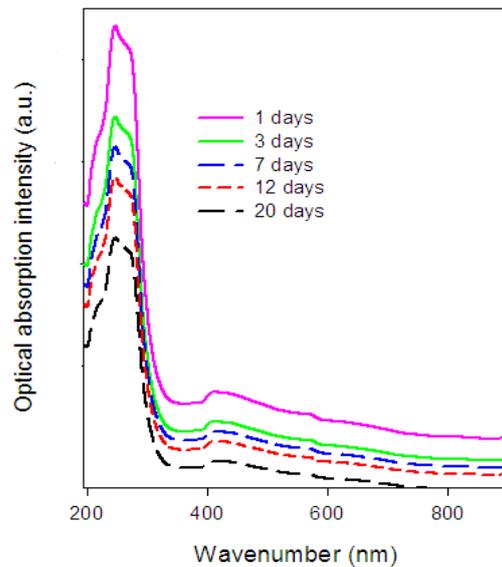


Fig. 9 Fading curve of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 500oC (G500) during 20 days at room temperature (25oC)

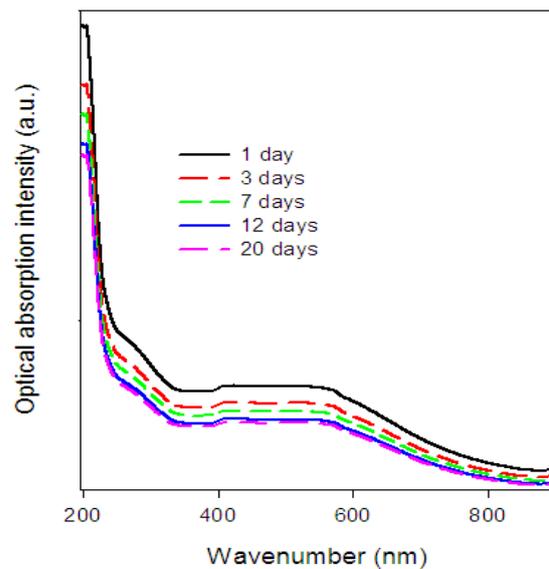


Fig. 10 Fading curve of silica gel doped with 1 (%) Nd<sup>3+</sup> ions sintered at 1150oC (G1150) during 20 days at room temperature (25oC)

#### 5) Energy Gap

The values of optical energy gap  $E_g$  are achieved by extrapolation of the line or region of the plots of  $(\alpha h\nu)^{1/2}$  against  $h\nu$  as shown in Figs. 11&12. It is observed that, there is an exponential increase in the absorption towards the edge and in all the cases the edge is not sharply described, signifying the glassy nature of the samples. The results listed in Table 1 show that the values of  $E_g$  decrease with increasing  $\gamma$ -irradiation dose. This in turn allocates us to conclude that the absorption mechanism involves indirect optical transition, or it may be due to the fact that the increase of  $\gamma$ -ray dose increases the spin density and the density of the unpaired electron in the unfilled bands, also the band tailing might be so pronounced as to result in the decrease in the

## A Comparison of Modifications Induced by Heat-Treatment and $\gamma$ -Irradiation in Spectroscopic Properties of Silica-Gel Thin Film Doped with Nd2O3

forbidden energy gap. It is well known that, [47] after irradiation, the defect centers formed by charge trapping of the radiolytic electrons or holes regularly have electronic states in the gap between the valence and conduction bands. Hence optical photons may induce transition between the valence band and the defect levels, or from the defect levels to excited states or the conduction band. In principle, the optical band of a defect center could be extremely narrow and well defined, but site-to-site variation arising from the random nature of the sol-gel glass invariably causes a distortion in the energy-level positions and a broadening of the band. In addition, the measured spectrum usually consists of one or more broad bands due to different color centers, and the bands often overlap. The shift of the absorption edge to a longer wavelength and the decrease of  $E_g$  to lower energies with an increase of irradiation dose are related to the progressive increase in the concentration of NBOs. This increase gives rise to a possible decrease of BOs. It is probable that for the same reason of the increase in NBOs, the  $E_g$  value shows a tendency to decrease with irradiation doses [48]. The real UV absorption is limited by extrinsic charge transfer absorption bands due to neodymium metal ions consisting of  $Nd^{3+}$  &  $Nd^{4+}$ . This absorption is shifted to higher energy due to the charge transfer bands of both  $Nd^{3+}$  and  $Nd^{4+}$ , which absorb UV photon and lose an electron to form stabilized  $(Nd^{3+})^+$  defect hole centers. Then the electron is trapped, forming silicon related induced electron centers [45].

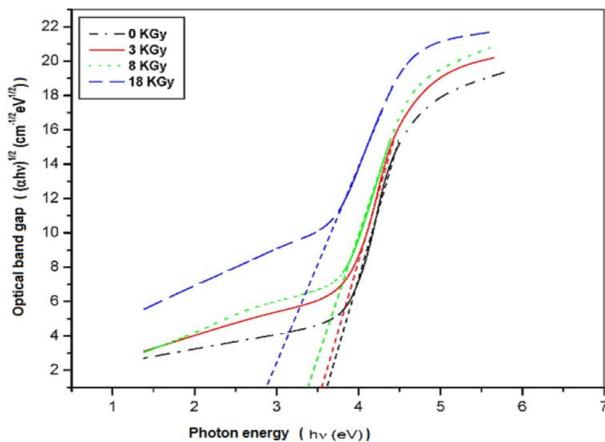


Fig. 11 Dependence of optical band gap  $(\alpha h\nu)^{1/2}$  on photon energy ( $h\nu$ ) for silica gel doped with 1 (%)  $Nd^{3+}$  sintered at 500oC (G500) sample.

Table 1. Effect of different  $\gamma$ -irradiation doses on the optical energy gap ( $E_g$ ) and Urbach energy ( $\Delta E$ ) of silica gel doped with 1 (%)  $Nd^{3+}$  ions sintered at 500 (G500) and 1150oC (G1150) samples.

Sample	$E_g$ (eV)				$\Delta E$ (eV)			
	0kGy	3kGy	8kGy	18kGy	0kGy	3kGy	8kGy	18kGy
G <sub>500</sub>	3.623	3.553	3.380	2.898	0.573	0.525	0.540	0.224
G <sub>1150</sub>	4.912	4.173	4.229	4.284	0.239	0.162	0.282	0.337

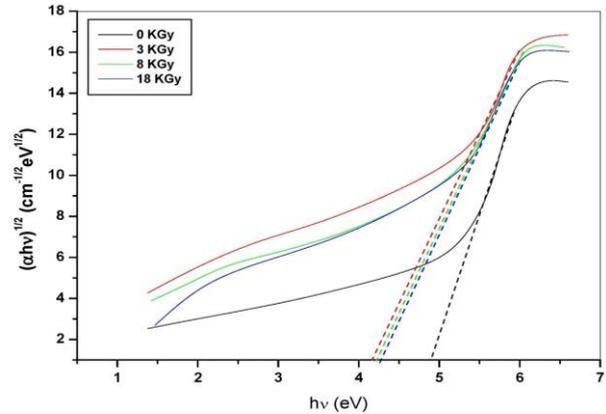


Fig. 12 Dependence of optical band gap  $(\alpha h\nu)^{1/2}$  on photon energy ( $h\nu$ ) for silica gel doped with 1 (%)  $Nd^{3+}$  sintered at 1150oC (G1150) sample.

### C. FTIR MEASUREMENTS

#### 1) Effect of Different Heat-Treatments

Neodymium metal ions have been used in glasses for their luminescence properties or as probes to follow the structural evolution of the host matrix[49,50]. The FTIR absorbance curve of samples G500 and G1150 extending from 400-4000  $cm^{-1}$  region has been studied and shown in Fig. 13. The bands at about 3300, 3670 and 3775  $cm^{-1}$  correspond to the fundamental vibrations of different hydroxyl groups. The presence of adsorbed water is indicated by the absorption band at 1540  $cm^{-1}$ , which is assigned as bending mode of water molecules. The characteristic bands at 975 and 1080  $cm^{-1}$  are due to asymmetric stretching vibrations peaks of Si-O-Si. The bending mode at 465  $cm^{-1}$  can be assigned to bending vibrations involving O-Si-O and Si-O-Si, characteristic of the three-dimensional network of silicate glasses [51-54]. However, the 700 and 800  $cm^{-1}$  vibration peaks are associated with symmetric stretching or vibrational modes of ring structures [55,56]. Other than, when the sample was sintered at 1150oC, many discrete bands appeared between the 482 and 950  $cm^{-1}$ . The absorptions at 792  $cm^{-1}$  are associated with symmetric O-Si-O stretching or vibrational modes of ring structures. In low wavelength region of FTIR spectrum, the band centered at 685  $cm^{-1}$  may be assigned to Nd-OH bond. The weak band at 625  $cm^{-1}$  was assumed to be related to the metal-oxygen peak[57]. The characteristic band of neodymium silicate appeared around 950  $cm^{-1}$  may be explained by the absorption due to asymmetric stretching mode vibration of Si-O-Nd band. However, Ono and Katsumata[58] reported that asymmetric stretching mode vibration of Si-O-Nd appears at 900  $cm^{-1}$ . The shifting of the Si-O-Nd band toward higher spatial frequency (1096 $cm^{-1}$ ) can be related to the large ionic radius of Nd ions. Though, recently Duhan[59] reported that asymmetric stretching mode vibration of Si-O-Nd appears at 906  $cm^{-1}$ . In addition, the slightly shift towards a higher wavelength with increasing temperature can be assumed to increasing in NBOs.

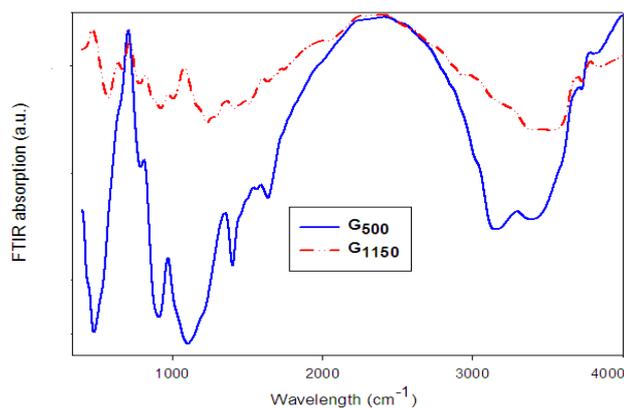


Fig. 13 Effect of two different sintering temperature on the FTIR absorption of silica gel doped with 1 (%) Nd<sup>3+</sup> sintered at 500oC (G500) and 1150oC (G1150) samples.

## 2) Effect of $\gamma$ -irradiation

It is to be mentioned that before irradiation it is very difficult to measure the thickness of the film, which is still in a gel state. In order to follow the polymerization and diols formation, we assumed that the number of C–H of CH<sub>2</sub> aliphatic bonds remained constant during the synthesis and polymerization. Therefore, the change in absorbance is monitored by normalizing to the absorbance of these C–H. After using an appropriate baseline correction of the two spectra before and after irradiation (Fig. 14), we have noticed an increase in the absorbance peaks at 3690 and 3765 cm<sup>-1</sup> after irradiation with shifting to shorter wavelength. This can be explained by accepting the assumption that with  $\gamma$ -irradiation, new bridging bond of Si–O–Nd is formed due to strongly polarizing Nd<sup>3+</sup> ions. As expected, after irradiation the peaks at about 850 cm<sup>-1</sup> and 880 cm<sup>-1</sup> decrease (of 44% and 47%, respectively), some epoxy rings disappear during  $\gamma$ -irradiation. There is a little increase of the vibration (about 2%) at 700 cm<sup>-1</sup>. It could be correlated with the diols formation during irradiation.

Irradiation effects in solids depend upon the energy of irradiation as well as on the nature of irradiating species [60]. In heavily disordered materials like glasses it is expected that radiation induced disturbances which are easily absorbed. High energy radiations like gamma rays change the spectral as well as structural defects called color centers of the materials. Fig. 14 shows the FTIR spectra of sample G500 after been exposed to 18kGy  $\gamma$ -ray irradiation. A number of structural changes could be assumed to be formed in the network as a result of irradiation. It is due to the bonding mechanisms of the formation of non bridging oxygens. Moreover silicon-oxygen bond is strongly affected by irradiation. As a result of gamma irradiation the vibrational modes H<sub>2</sub>O and H OH bending mode are extended. It is observed that on irradiation more stability is obtained due to the increase in number of oxygen ions available in the glass network. Hence more stable glasses with compact tetrahedral structures are assumed to be formed. The remarkable reduction of the absorption bands in the region between about 400 and 1685cm<sup>-1</sup> after  $\gamma$ -irradiation, which can be related to the fundamental stretching vibrations of different hydroxyl

groups, may be explicated by the condensation of first Si–OH groups leading to Si–O–Si links and second C–OH groups leading to C–O–C bands. Adding together, radiation dose (18 kGy) may be is not enough to evacuate OH groups and the inorganic part becomes suitably rigid to form a real trap for the remaining OH groups, avoiding their evacuation. The overall effects of gamma irradiation on the IR spectra are visualized by the maintenance of the number and position of the main IR bands observed in the glasses before irradiation and only minor variations in the intensity of some bands are identified after irradiation and the results are the same as shown in Fig. 14. Some scientists have reached to the same observations in other different glasses [61, 62], and they have related them to the weakening of the already non-periodic network structure or to changes in the bond angles and/or bond lengths between the building structural units as recently suggested by various authors. The observed results can thus be interpreted by assuming that gamma irradiation causes some variations in the bond angles and/or bond lengths within the structural groups as suggested before.

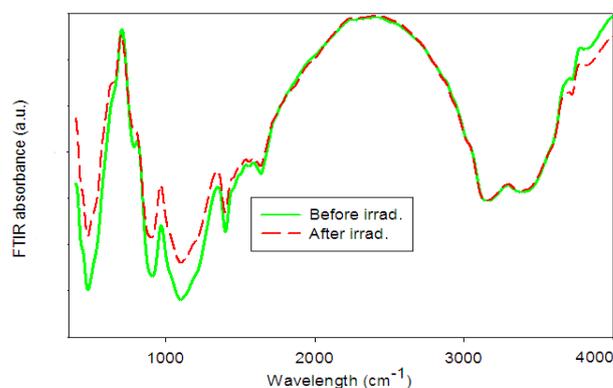


Fig. 14 Effect of irradiation dose (18 kGy) on the FTIR absorption of silica gel doped with 1 (%) Nd<sup>3+</sup> sintered at 500oC (G500) sample.

## III. CONCLUSION

This study aims at developing glass easily affected by successive heat-treatment and  $\gamma$ -irradiation doses. Neodymium oxide was added as activator in order to examine the effects of  $\gamma$ -irradiation on the structural and optical properties, a detailed systematic study of Nd<sub>2</sub>O<sub>3</sub> thin films has been carried out, by applying different amounts of irradiation on different substrates. The amorphous nature of gel glasses have been confirmed by XRD spectra at different temperatures. The behavior of both optical absorption and transmission spectra of the irradiated samples indicates a strong dependence with gamma radiation doses, where the magnetic dipole transition <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> of the Nd<sup>3+</sup> ions presents huge defects for irradiation doses up to 18 kGy. Optical absorption and transmission % spectra have been studied before and after  $\gamma$ -irradiation in order to understand the changes in the optical properties of glasses as well as to find the characteristics frequencies of the vibrational modes of chemical bonds, which decide the structural and spectral changes. As a result, the number of ion-trapping sites may increase due to the defect centers. Therefore, more protons accumulate in irradiated Nd<sub>2</sub>O<sub>3</sub> thin films. In contrast  $\gamma$ -irradiation shows decrease in transmission% for all the whole spectrum lines and is ~ 90% quenched at

# A Comparison of Modifications Induced by Heat-Treatment and $\gamma$ -Irradiation in Spectroscopic Properties of Silica-Gel Thin Film Doped with Nd2O3

around 1150°C. The optical energy gap  $E_g$  was found to decrease with the increase of the irradiation doses, it is suggested that the mechanism of optical transition is forbidden by indirect transition. The FTIR spectra reveal the bonding system of the constituent atoms and groups such as Si-O, and OH that throw light to the expected structure. The FTIR spectra have shown that high temperature heat treatment can greatly reduce the amount of OH groups and the organic residues in the silica glass but the amount of hydroxyl group in the dense glass is still significant causing weak intensity. However,  $\gamma$ - irradiation produces minor effect on the IR spectra which can be related to the shielding behavior of the glass. The large absorption enhancement presented by these ions ( $Nd^{3+}$ ) when exposed to  $\gamma$ - radiation, strongly suggests that these materials are of great potential for use as radiation detectors. Also, our results show that a high temperature sintering treatment would be necessary to reduce efficiently the hydroxyl content.

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